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Force constants and mean amplitudes of vibration of some octahedral water complexes of Mg, Al, Ni and Zn

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The seven parameter modified Urey-Bradley force constants and General Quadratic potential force constants have been evaluated for $Mg(H_2O)_6$, $Al(H_2O)_6$, $Ni(H_2O)_6$ and $Zn(H_2O)_6$. The constants have been compared with the reported values of GVFF constants and are found to be in good agreements. Mean amplitudes of vibration and generalised mean square amplitudes are computed at three temperatures ($T = 0°K$, 298°K and 500°K) using Cyvins method. The results are discussed in the light of physical parameters of central atom

INTRODUCTION

In an earlier communication (Sanyal *et al* 1969), we have reported the vibrational mean amplitude values of some pyramidal $M(CH_3)_3$ type systems (where M = N, P, Sb, As and Bi), assuming the end group as a *point mass*. Recently, normal coordinate analysis of $P(CH_3)_3$ has been done by Smith and Dijkstra (1971) and this has confirmed the validity of our assumption. Now vibrational frequencies (Ananthanarayanan & Danti 1970) are available for some octahedral water complexes of $M(H_2O)_6$ type where M = Mg, Al, Zn and Ni. Detailed spectroscopic studies of these systems have been carried out by Ananthanarayanan (1961, 1962, 1966, 1968) The octahedral systems of XY (O_h) type have been studied extensively by several workers (Ananthanarayanan 1968, Pandey *et al* 1969, Sanyal *et al* 1970, Thakur & Rai 1966, Rao *et al* 1970) due to its high symmetry In the present communication, the normal coordinate analysis has been carried out for four water complexes assuming end group as the point mass of 18.01534.

The six fundamental vibrations presented in table 1 are ν_1 (A_{1g} totally symmetric), ν_2(E_g doubly degenerate), ν_3 and ν_4 (F_{1u} triply degenerate and active in I R. absorption only), ν_5 (F_{2g} triply degenerate active in Raman effect only), ν_6(F_{2u} triply degenerate). These reported frequencies for $M^I(H_2O)_6$ where M^I = Mg, Zn, or Ni are average values of $M^I(SO_4)7H_2O$, $K_2M^I(SO_4)_2$ $6H_2O$ and $M^I(NH_4)_2$ $6H_2O$. The values used for $Al(H_2O)_6$ are the average values reported for K-alum and NH_4-alum and some are estimated.

Table 1. Vibrational frequencies in (cm^{-1}) for octahedral water complexes of Mg, Zn, Al and Ni

Systems	A_{1g}-ν_1	E_g-ν_2	F_{1u}-ν_3	F_{1u}-ν_4	F_{2g}-ν_5	F_{2u}-ν_6
$Mg(H_2O)_6$	370	205	499	268	253	134
$Al(H_2O)_6$	324	196	418	240	236	112
$Ni(H_2O)_6$	404	257	392	296	251	134
$Zn(H_2O)_6$	393	200	378	275	267	147

Theoretical Considerations

In the evaluation of molecular constants, the symmetry elements and F-G matrix elements were taken from literature (Kimura & Kimura 1963, Decius 1959, Asprey *et al* 1970). These elements have been used in our earlier computations (Pandey *et al* 1969, Sanyal *et al* 1970) and have recently also been applied by Asprey *et al* (1970). Although, modified Urey-Bradley force field has been applied in the case of many octahedral systems (Venkateswarlu & Sundaram 1956, Sanyal & Dixit 1972, Hiraishi *et al* 1964, Kim *et al* 1968), no such study has been made in the case of octahedral water complexes possibly due to their limited spectral data. In the present work an attempt has been made to examine the nature of forces in these systems using modified seven parameter Urey-Bradley force field introduced by Venkateshwarlu et al (1968) and general quadratic potential field given by Pistorius (1958) The second order secular equation $FG-\lambda E = 0$ for F_{1u} species have been solved by the approximation given by Krebs & Muller (1968) The G and F matrix elements used in both the force fields are as follows

Species	G-matrix	F-matrix elements GQPF	MUBFF
A_{1g}	$G_{11} = \mu_y$	$F_{11} = f_{dd}+4f_{d\delta}+f'_{dd}$	$K+4F+k$
E_g	$G_{11} = \mu_y$	$F_{11} = f_d-2f_{dd}+f'_{dd}$	$K+F+3F'+k$
F_{1u}	$G_{11} = 2\mu_x+\mu_y$	$F_{11} = f_d-f'_{dd}$	$K+2F+2F'-k$
	$G_{12} = G_{21} = -4\mu_x$	$F_{12} = F_{21} = 2(f_{d\delta}-f_{d\alpha})$	$F+F'$
	$G_{22} = 8\mu_x+2\mu_y$	$F_{22} = f_\alpha+2f_{\alpha\alpha}-2f''_{\alpha\alpha}-f'''_{\alpha\alpha}$	$H+F/2-3/2F''+2h$
F_2	$G_{11} = 4\mu_y$	$F_{11} = f_\alpha-2f'_{\alpha\alpha}+f''_{\alpha\alpha}$	$H+F/2-F''/2-2g$
F_1	$G_{11} = 2\mu_y$	$F_{11} = f_\alpha-2f_{\alpha\alpha}+2f'_{\alpha\alpha}-f'''_{\alpha\alpha}$	$H+F/2+F''/2-2h$

where μ_i is the reciprocal mass of i-th atom, f_d is the bond stretching force constant and f_α is the interbond deformation constant. The rest are interaction constants which refer to the various pairs of coordinates.

Cyvin's fundamental secular equation $|\Sigma G^{-1} - \Delta E| = 0$ has been solved to get symmetrized mean square amplitudes of vibration, where G is the kinetic energy matrix and E the unitary matrix and Δ_i is related to the normal frequencies ν_i by the relation :

$$\Delta_i = \frac{h}{8\pi^2 c \nu_i} \coth \left(\frac{h \nu_i c}{2kT}\right)$$ where T is the absolute temperature and k is the Boltzmann constant. Using the relations given by Bye & Cyvin (1963), the generalized mean square amplitudes and mean amplitudes of vibration have been evaluated at three temperatures, T = 0°K, 298°K and 500°K for bounded as well as non-bounded distances

Results and Discussion

Results obtained by MUBFF and GQPF force fields are presented in table 2 and 3 respectively. In table 3 the values in parenthesis are GVFF force constants

Table 2. MUBFF constants in (mdyn/Å) for octahedral water complexes of Mg, Zn, Al and Ni

Systems			H			F'	g
$Mg(H_2O)_6$	0 632	0.279	−0.033	0.012	−0.265	−0.064	−0 018
$Al(H_2O)_6$	0.486	0.199	−0 013	0.001	−0 169	−0.036	−0.015
$Ni(H_2O)_6$	0 702	0.272	0 008	0 006	−0.059	−0 071	−0.006
$Zn(H_2O)_6$	0.629	0.286	−0.028	−0.029	−0 133	−0.119	−0 014

Table 3. Comparison of force constants obtained by GQPF and GVFF* (mdyn/Å)

Systems	Force field	$(f_d+f'_{dd})$	f_{dd}	$(f_{d\alpha}-f_{d\alpha''})$	$(f_\alpha-f_{\alpha\alpha'''})$	$(f_{\alpha\alpha}-f_{\alpha\alpha''})$	$(f_\alpha-f_{\alpha\alpha'})(f_{\alpha\alpha'}-f_{\alpha\alpha'''})$	
$Mg(H_2O)_6$	GQPF	0 782	0.168	0.104	0.134	0.019	0.142	−0.018
	GVFF*	0.781	0 168	0 253 or 0.039	0 329 or 0.169	0.117 or 0.037	0.250 or 0.169	0 080 or −0.0004
$Zn(H_2O)_6$	GQPF	0 829	0.202	0 983	0.175	0 030	0.188	−0 014
	GVFF*	0 830	0 202	0.183 or 0.035	0 276 or 0.198	0.080 or 0.042	0.239 or 0.200	0.037 or −0.002
$Al(H_2O)_6$	GQPF	0.643	0.118	0 082	0.104	0.019	0.126	−0.022
	GVFF*	0.641	0.117	0.197 or 0.036	0.242 or 0.125	0.088 9r 0.029	0.195 or 0.136	0.047 or −0.011
$Ni(H_2O)_6$	GQPF	1.045	0.172	0.100	0.179	0.042	0.185	−0.006
	GVFF*	1.046	0.172	0 216 or 0 072	0.265 or 0 185	0.085 or 0.045	0.216 or 0.176	0.049 or 0.008

* Taken from Ananthanarayanan & Danti 1970.

reported by Ananthanarayanan & Danti (1970). The results of generalized mean square amplitudes and mean amplitudes of vibration for different systems and different distances are given in tables 4 and 5.

A comparison of the stretching force constants shows that the results obtained by both the force fields are in reasonable agreement with those of GVFF values reported by Ananthanarayanan & Danti. The stretching force constants K increase with the increase in atomic weight of X-atom in the same group as seen in the case of Mg(II A group) and Zn (II B group). In the case of Al (III A group) and Ni (VIII group), as the mass of central atom increases the same trend is observed, even though they do not fall in the same group. Thus, the stretching force constant for the central atom of the same group follows the reverse trend of single bond metallic radii (Pauling 1970) *e.g.* Mg (1.364) > Zn (1.249). A comparison for Al and Ni would have been possible if other systems of the same group were available. Since metallic radii of Zn and Al are nearly equal, the GVFF stretching constants have nearly same value. Also the interaction constants evaluated by both force fields are reasonably comparable with those of GVFF constants Among the dual values reported for interaction constants (GVFF),

Table 4 Generalized mean square amplitude quantities (in 10^{-4}Å^2) of some $M(H_2O)_6$ type systems

Distance	Symbol	$Mg(H_2O)_6$			$Zn(H_2O)_6$		
		T = 0°K	T = 298°K	T = 500°K	T=0°K	T = 290°K	T=500°K
M—(H_2O)	$<\Delta z^2>$	42 702	67 098	102 616	3 363	66.722	102 165
	$<\Delta x^2>$	54 153	119 905	183.765	42 322	91.419	145.088
	$<\Delta y^2>$	54.153	119 905	183 765	42.322	91 419	145.088
(H_2O)...(H_2O)	$<\Delta z^2>$	77 720	156 459	259 252	78.255	160 568	253.783
(linear)	$<\Delta x^2>$	36.980	67 902	106 056	33.902	58 200	89 818
	$<\Delta y^2>$	36 980	67 902	106 056	33 902	58 200	89 818
(H_2O)...(H_2O)	$<\Delta z^2>$	123 050	225.468	388 820	103 126	179 562	277.128
(non-linear)	$<\Delta y^2>$	88 323	257 352	419.694	80 981	215 728	350 353

		$Al(H_2O)_6$			$Ni(H_2O)_6$		
M—(H_2O)	$<\Delta z^2>$	46.867	77 616	117 564	28 837	53.249	83.760
	$<\Delta x^2>$	60 240	40.644	239 854	43 867	99.506	197.112
	$<\Delta y^2>$	60 240	140.644	239 854	43 867	99.506	197.112
(H_2O)...(H_2O)	$<\Delta x^2>$	82 908	137.752	274.927	63 987	108.600	183 953
(linear)	$<\Delta x^2<$	39.749	76.968	121.208	37.278	68.876	07 693
	$<\Delta y^2>$	39 649	76 968	121.208	37 278	68.876	107 683
(H_2O)...(H_2O)	$<\Delta z^2<$	143.769	155.060	346.601	100.495	183.960	324.587
(non-linear)	$<\Delta x^2>$	130.232	153.354	400.574	96.091	161 282	294.462
	$<\Delta y^2>$	103.372	354.954	583.687	94.469	257.775	420.508

Table 5. Mean amplitudes of vibration of $M(H_2O)_6$ type systems in Å

Systems	Distance	$T = 0°K$	$T = 290°K$	$T = 500°K$
$Mg(H_2O)_6$	Mg—(H_2O)	0.065	0.082	0.101
	(H_2O)...(H_2O) (linear)	0.088	0.125	0.161
	(H_2O)...(H_2O) (non-linear)	0 111	0.150	0.197
$Zn(H_2O)_6$	Zn—(H_2O)	0.057	0.081	0 119
	(H_2O)...(H_2O) (linear	0.088	0 127	0 159
	(H_2O)...(H_2O) (non-linear)	0.102	0 134	0.166
$Al(H_2O)_6$	Al—(H_2O)	0.068	0.088	0.0108
	(H_2O)...(H_2O) (linear	0.091	0 117	0.166
	(H_2O) ..(H_2O) (non-linear)	0 119	0.124	0 186
$Ni(H_2O)_6$	Ni—(H_2O)	0.054	0 073	0 092
	(H_2O).. (H_2O) (linear)	0.080	0 104	0.136
	(H_2O) ..(H_2O) (non-linear)	0.100	0.136	0.180

the second set of values seems to be more reasonable as reported by Ananthanarayanan & Danti (1970). This is confirmed by GQPF constants also, since they are comparable both in magnitude and sign to the second set. In some cases, the interaction constants lie in-between the reported dual values. The order of electronegativity of central atoms for systems under study is Zn > Mg and Ni > Al and this order is followed by the stretching force constants, and consequently by interaction force constants, between two perpendicular bonds in the same plane.

Examining the generalized mean square parallel amplitude of vibration $<\Delta z^2>$ and generalized mean square perpendicular amplitudes $<\Delta x^2>$ and $<\Delta y^2>$, it is seen that they increase with the increase of temperature. Similarly, the mean amplitudes of vibration (table 5), (σ_r) due to bounded M...(H_2O) group, (σ_d) due to non-bonded, non-linear (H_2O)—(H_2O) and ($\sigma d'$) due to nonbounded linear (H_2O)...(H_2O) group show same variations with temperature.

From the table it is evident that the mean amplitude of vibration for bonded and non-bonded distances are in the order M-(H_2O) < (H_2O)...(H_2O) linear <(H_2O)...(H_2O) non-linear.

From the table it appears that as the electronegativity of central atoms decreases the mean ampliude of vibration increases. Thus, it may be concluded that for stronger bonds, the mean amplitudes of vibrations are smaller. The estimated values of mean amplitudes of vibration from electron diffraction data for any of the systems under study is not available and hence no comparison could be made. However, the results of the present investigation will be helpful for the interpretation of electron diffraction results and provides an opportunity to test the experimental results.

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